Los Alamos
NATIONAL LABORATORY
EST. 1943

*Environmental Programs*
P.O. Box 1663, MS M991
Los Alamos, New Mexico 87545
(505) 606-2337/FAX (505) 665-1812




*National Nuclear Security Administration*
Los Alamos Site Office, MS A316
Environmental Restoration Program
Los Alamos, New Mexico 87544
(505) 667-4255/FAX (505) 606-2132

*Date:* NOV 13 2009
*Refer To:* EP2009-0560

James Bearzi, Bureau Chief
Hazardous Waste Bureau
New Mexico Environment Department
2905 Rodeo Park Drive East, Building 1
Santa Fe, NM 87505-6303

**Subject: Corrections to Tritium Pore-Vapor Concentration Data**

Dear Mr. Bearzi:

Los Alamos National Laboratory (LANL) technical staff met with the New Mexico Environment Department (NMED) Hazardous Waste Bureau representatives on September 15, 2009, to review the technical basis for correcting underreported tritium pore-vapor concentrations. Per NMED's request, LANL is providing the following technical information in a report accompanying this letter (Attachment 1):

- documentation of the low bias
- method for correction
- correction methods for pre-July 2009 data
- updates to LANL environmental database

In addition, Attachment 2 lists the reports submitted to NMED before July 26, 2009, that include uncorrected data. The technical documents referenced in this letter are included as Attachments 3 and 4.

All LANL reports containing tritium pore-vapor data submitted to NMED after July 26, 2009, contain corrected values. All tritium pore-vapor data in the LANL environmental database and the RACER database have been corrected. Because corrected tritium pore-vapor data are available through the RACER database, NMED has agreed that LANL does not need to revise reports submitted before July 26, 2009, that contained uncorrected tritium pore-vapor data.

If you have any questions, please contact Jean Dewart at (505) 665-0239 (dewart@lanl.gov) or David Gregory at (505) 667-5808 (dgregory@doeal.gov).

Sincerely,

Michael J. Graham, Associate Director
Environmental Programs
Los Alamos National Laboratory

Sincerely,

David R. Gregory, Project Director
Environmental Operations
Los Alamos Site Office

MG/DG/CE/JD:am

Attachments:
(1) Correction of Tritium Pore-Vapor Concentrations for the Impacts of Silica Gel–Bound Water (LA-UR-09-6434)
(2) Documents Submitted to NMED Containing Uncorrected Tritium Pore-Vapor Data
(3) Technical Implementation of the Correction Factor Calculation for Tritium in Pore-Gas Data, Revision 1 (LA-UR-09-6972)
(4) Corrections for Measurements of Tritium in Subterranean Vapor Using Silica Gel (LA-UR-09-6230)

Cy: (w/att)
Laurie King, EPA Region 6, Dallas, TX
Steve Yanicak, NMED-DOE-OB, MS M894
David Gregory, DOE-LASO, MS A316
Debbie Nevergold, ADEP-ET, MS M992
Craig Eberhart, WES-EDA, MS M992
Kristine Smeltz, EP-WES, MS M992
RPF, MS M707

Cy: (w/o enc.)
Tom Skibitski, NMED-OB, Santa Fe, NM
Annette Russell, DOE-LASO (date-stamped letter emailed)
Michael J. Graham, ADEP, MS M991
Alison M. Dorries, EP-WES, MS M996
Chris Echohawk, WES-EDA, MS M992
Karen Schultz-Paige, WES-EDA, MS M992
IRM-RMMSO, MS A150 (date-stamped letter emailed))

**Attachment 1**
**Correction of Tritium Pore-Vapor Concentrations for the Impacts of Silica Gel–Bound Water**


Summary

As part of a review of the environmental sampling procedures, Los Alamos National Laboratory (LANL) identified a low bias in the tritium pore-vapor concentration data caused by the inherent properties of silica gel, the sampling medium. The bias can be corrected through the use of field data collected for each sample. Standard Operating Procedure 5074, Sampling of Sub-Atmospheric Air, has been revised to ensure the collection of the field data required the correction. The LANL environmental database has been updated to use the field data to correct for the low bias. All tritium pore-vapor concentration data, including pre-July 2009 samples, have been corrected in the LANL environmental database. Corrected tritium pore-vapor concentration data are available to the New Mexico Environment Department (NMED) and the public through the RACER database. Reports submitted to NMED after July 26, 2009, include corrected data.

This letter provides the documentation of the low bias, the method for correction, the corrections for pre-July 2009 data, updates to databases, and a list of reports submitted to NMED before July 26, 2009, that include uncorrected data. Also attached are the two technical documents referenced in this letter.


Low bias in tritium pore-vapor concentrations

Pore gas samples are pulled through a canister containing silica gel, a desiccant that absorbs water vapor from the pore-gas sample. At the end of sampling, water is distilled from the silica gel at the analytical chemistry laboratory. The sample water is analyzed for tritium using liquid scintillation counting techniques.

Silica gel contains water bound to the silica gel molecules at the beginning of sampling, which cannot be removed from the silica gel by drying before sampling. As the pore-vapor sample is pulled through the silica gel, the tritium in the pore-vapor sample is diluted by the "nontritiated" (or almost nontritiated) bound water of the silica gel (Whicker et al. 2009). Thus, the water sample distilled from the silica gel by the analytical laboratory at the end of sampling has a lower tritium concentration than the original pore-vapor sample.

A correction factor (CF), accounting for the dilution by silica gel bound water, can be determined on a sample-by-sample basis from the weight of the initial silica gel sample medium, the amount of moisture collected in the sample, and the bound water percentage of the silica gel (Whicker et al. 2009). The pore-vapor sample tritium concentration received from the analytical laboratory is then multiplied by the correction factor to account for the dilution by silica gel bound water.

$$CF = \frac{[SGi * BW] + MS}{MS} \qquad \textbf{Equation 1}$$

SGi = weight of dry silica gel in grams

BW = silica gel–bound water fraction

MS = weight of sample moisture water collected in grams

Correction of tritium pore-vapor concentrations (July 2009 and after)

For each tritium pore-vapor sample, the initial weight of the silica gel, the initial weight of the sample canister, and the final weight of the sample canister (following sampling) are measured. These data are entered into the database along with the fraction of bound water. Silica gel is routinely tested to determine the bound-water fraction. Typical bound-water values found in the literature are 0.05 to 0.07. The mean bound-water fraction in silica gel used in LANL tritium pore-vapor monitoring is 0.064 (Whicker et al. 2009). The database calculates the correction factor for each sample based on these parameters and then calculates a corrected tritium pore-vapor concentration using the correction factor and the tritium pore-vapor concentration result from the analytical laboratory. The individual sample uncertainty value and minimum detectable activity are also corrected using this same method.

This method of correction assumes the water bound to the silica gel before sampling contains no tritium. In fact, naturally occurring tritium can be detected in water of about 27 pCi/L (NCRP 1979; UNSCEAR 2000). For tritium pore-vapor sample values at or near background levels, the correction factor overestimates the true concentration.

Correction of pre-July 2009 data

Tritium pore-vapor data have been collected routinely since 2001. To provide a consistent set of tritium pore-vapor data (pre and post July 2009 data) for use in potential data assessment tasks (e.g., contaminant transport and diffusion modeling), LANL has corrected all tritium pore-vapor data collected before July 2009. To correct pre-July 2009 data, LANL used the percent moisture values available from the analytical chemistry laboratory, since the field data were not required to be collected and hence is not available. Analytical laboratory percent moisture data are available for more than 90% of pre-July 2009 data.

The analytical laboratory reports a percent moisture value for each tritium pore-vapor sample (Marczak 2009). The percent moisture value is calculated by the analytical laboratory as the moisture collected from the sample divided by the weight of the dry silica gel plus the moisture collected from the sample (i.e., MS/(SGi+MS)). Using the percent moisture value, expressed as a fraction, Equation 1 can be transformed to

$$CF = [(1/\%\ \text{Moisture}) - 1] * BW + 1 \qquad \textbf{Equation 2}$$

Some pre-July 2009 samples have no analytical laboratory percent moisture values. An estimate of the distribution of correction factors has been calculated (Whicker et al. 2009). Based on a review of 2 yr of tritium pore-vapor sample field data, the minimum, median, and maximum values of the correction factor are 1.14, 1.43, and 5.27, respectively (Whicker et al. 2009). Ninety-five percent of the correction factor values were less than about 2. Thus, when analytical laboratory percent moisture values were not available, tritium pore-vapor concentrations were corrected using a factor of 2 for pre-July 2009 data.

Updates to LANL environmental database

The LANL environmental database has been updated to store silica gel field data and to calculate corrected tritium pore-vapor concentrations following Equation 1. The database also calculates the corrected individual sample uncertainty and minimum detectable activity values using this same method.

The corrected tritium pore-vapor concentration is uploaded into the RACER database. The original analytical laboratory tritium pore-vapor concentration (uncorrected value) remains in the LANL environmental database and is available upon request.

To document the method of correction used for individual tritium pore-vapor samples, qualifier reason codes have been added to the environmental database and/or comments have been added to the environmental database Chemical Analysis Result (CAR) table.

| Method for Calculating Correction Factor | Validation Reason Code | Qualifier Reason Code | Comment in CAR table (appended to existing comment) |
|---|---|---|---|
| Silica gel field weights for the individual sample | No change from original sample | No change from original sample | No comment code related to tritium correction factor |
| Percent moisture value from analytical laboratory for the individual sample | No change from original sample | No change from original sample | R17A = data have been recalculated to reflect bound water using percent moisture |
| Silica gel field weights and analytical laboratory percent moisture are not available. Correction factor of 2 is used. | "J" added to existing qualifier | R17 | R17B = data have been recalculated to reflect bound water using factor of 2 |

Reports submitted to NMED before July 26, 2009

LANL has submitted a number of reports to NMED between 1994 and 2009 that include tritium pore-vapor data, which are not corrected. These reports are listed in the attached table. None of these uncorrected data were used in making regulatory decisions (e.g., no further action). All the data published in these reports are now corrected and available through the RACER database.

References

Marczak, S., October 2009. "Technical Implementation of the Correction Factor Calculation for Tritium in Pore-Gas Data, Revision 1," Los Alamos National Laboratory document LA-UR-09-6972, Los Alamos, New Mexico. (Marczak 2009)

NCRP (National Council on Radiation Protection). 1979. Tritium in the Environment. NCRP Report no. 62.

UNSCEAR (United Nations Scientific Commission on the Effects of Atomic Radiation). 2000. Report of the United Nations Scientific Committee on the Effects of Atomic Radiation to the General Assembly.

Whicker, J.J., J.M. Dewart, S.P. Allen, W.F. Eisele, M.C. McNaughton, and A.A. Green, September 2009. "Corrections for Measurement of Tritium in Subterranean Vapor Using Silica Gel," Los Alamos National Laboratory document LA-UR-09-6230, Los Alamos, New Mexico. (Whicker et al. 2009)

## Attachment 2
## Documents Submitted to NMED Containing Uncorrected Tritium Pore Vapor Data

| Document Title | Date Submitted | Document Catalog Number | LA-UR Number |
|---|---|---|---|
| **MDA A** | | | |
| Investigation Report (MDA A) | 11/09/06 | EP2006-0835 | LA-UR-06-7902 |
| Status Report for Supplemental Sampling at Material Disposal Area A, Technical Area 21, Summarizing Results of Additional Field Work | 12/05/07 | EP2007-0748 | LA-UR-07-8107 |
| Corrective Measures Evaluation Report for Material Disposal Area A, Solid Waste Management Unit 21-014, at Technical Area 21 | 09/02/08 | EP2008-0448 | LA-UR-08-5520 |

| Document Title | Date Submitted | Document Catalog Number | LA-UR Number |
|---|---|---|---|
| **MDA C** | | | |
| IWP for MDA C | 07/31/03 | ER2003-0338 | LA-UR-03-3803 |
| IWP RSI Response, and Revision 1 (MDA C) | 11/07/03 | ER2003-0696 | LA-UR-03-8201 |
| IWP for MDA C, Revision 2 | 10/21/05 | ER2005-0172 | |
| Investigation Report for Material Disposal Area C, Solid Waste Management Unit 50-009, at Technical Area 50 | 12/06/06 | EP2006-1000 | LA-UR-06-8096 |
| Drilling and Sampling Results from Boreholes Between Pit 2 and Pit 3 at Material Disposal Area C, Solid Waste Management Unit 50-009, at Technical Area 50 | 04/19/07 | EP2007-0231 | |
| Pilot Test Investigation Report for Evaluating Vapor-Sampling Systems at Material Disposal Area C, Solid Waste Management Unit 50-009, at Technical Area 50 | 07/25/08 | EP2008-0389 | LA-UR-08-4814 |
| Phase II Investigation Report for Material Disposal Area C, Solid Waste Management Unit 50-009, at Technical Area 50 | 05/07/09 | EP2009-0215 | LA-UR-07-5083 |

| Document Title | Date Submitted | Document Catalog Number | LA-UR Number |
|---|---|---|---|
| **MDA G** | | | |
| MDA G IWP | 09/30/03 | ER2003-0279 | LA-UR-03-6491 |
| Reformatted IWP, Revision 1 (MDA G) | 06/22/04 | ER2004-0272 | LA-UR-04-3742 |
| Investigation Report for Material Disposal Area G, Consolidated Unit 54-013(b)-99, at Technical Area 54 | 09/08/05 | ER2005-0626 | LA-UR-05-6398 |
| Validated Data for Borehole 1 for the Investigation Report (MDA G) | 10/11/05 | ER2005-0626 | |
| Corrective Measures Evaluation Plan for Material Disposal Area G at TA-54 | 05/03/06 | ER2006-0211 | LA-UR-06-1709 |
| Periodic Monitoring Report for Vapor Sampling Activities at Material Disposal Area G, Solid Waste Management Unit 54-013(b)-99 at Technical Area 54 | 07/24/06 | EP2006-0471 | LA-UR-06-3708 |
| Addendum to the Investigation Report for Material Disposal Area G, Consolidated Unit 54-013(b)-99, at Technical Area 54 | 05/16/07 | EP2007-0215 | LA-UR-07-2582 |
| Corrective Measures Evaluation Plan for Material Disposal Area G, Solid Waste Management Unit 54-013(b)-99 at Technical Area 54, Revision 1 | 07/13/07 | EP2007-0393 | LA-UR-07-4591 |
| Corrective Measures Evaluation Plan for Material Disposal Area G at Technical Area 54, Revision 2 | 10/15/07 | EP2007-0630 | LA-UR-07-6882 |
| Periodic Monitoring Report for Vapor Sampling Activities at Material Disposal Area G, Technical Area 54, For Fiscal Year 2007 | 12/21/07 | EP2007-0772 | LA-UR-07-8192 |
| Corrective Measures Evaluation Report for Material Disposal Area G, Consolidated Unit 54-013(b)-99, at Technical Area 54 | 09/12/08 | | LA-UR-08-5781 |
| Periodic Monitoring Report for Vapor Sampling Activities at Material Disposal Area G, at Technical Area 54, for Fiscal Year 2008 | 12/18/08 | EP2008-0633 | LA-UR-08-7862 |
| Pilot Test Report for Evaluating FLUTe Vapor-Sampling Systems in Use at Material Disposal Area G | 08/20/08 | EP2008-0445 | LA-UR-08-5385 |
| Pilot Test Report for Evaluating Soil-Vapor Extraction at Material Disposal Area G at Technical Area 54, Revision 1 | 01/30/09 | EP2009-0067 | LA-UR-09-0565 |

| Document Title | Date Submitted | Document Catalog Number | LA-UR Number |
|---|---|---|---|
| **MDA H** | | | |
| Addendum to the RFI Report for Material Disposal Area (MDA) H, (Solid Waste Management Unit 54-004) at Technical Area (TA)-54 | 10/22/02 | ER2002-0682 | LA-UR-02-3397 |
| CMS Report (MDA H) | 05/30/03 | ER2003-0121 | |
| Monitoring Data (MDA H) | 04/15/05 | ER2005-0235 | |
| Corrective Measures Study Report for Material Disposal Area H, Solid Waste Management Unit 54-004, at Technical Area 54, Revision 1 | 06/30/05 | ER2005-0020 | LA-UR-05-0203 |
| Monitoring Data for First Two Quarters FY05 and Previous Sampling Data (MDA H) | 06/30/05 | | |
| Periodic Monitoring Report for Vapor Sampling Activities at Material Disposal Area H, Solid Waste Management Unit 54-004 at Technical Area 54 | 08/11/05 | ER2005-0547 | LA-UR-05-5446 |
| Periodic Monitoring Report for Vapor Sampling Activities at Material Disposal Area H, Solid Waste Management Unit 54-004 at Technical Area 54 | 12/12/05 | ER2005-0882 | |
| Periodic Monitoring Report for Vapor Sampling Activities at Material Disposal Area H, Solid Waste Management Unit 54-004 at Technical Area 54 | 06/09/06 | ER2006-0365 | LA-UR-06-3237 |
| "Periodic Monitoring Report for Vapor-Sampling Activities at Material Disposal Area H, Solid Waste Management Unit 54-004, at Technical Area 54 for the Second Quarter of Fiscal Year 2006" | 08/08/06 | EP2006-0689 | LA-UR-06-4976 |
| "Periodic Monitoring Report for Vapor-Sampling at Material Disposal Area H, Solid Waste Management Unit 54-004, at Technical Area 54 for the Third and Fourth Quarters of Fiscal Year 2006" | 11/28/06 | EP2006-0972 | LA-UR-06-8093 |
| Periodic Monitoring Report for Vapor-Sampling Activities at Material Disposal Area H, Solid Waste Management Unit 54-004, at Technical Area 54, Fiscal Year 2007 | 11/30/07 | EP2007-0716 | LA-UR-07-7803 |
| Periodic Monitoring Report for Vapor Sampling Activities at Material Disposal Area H, at Technical Area 54, Fiscal Year 2008 | 01/28/09 | EP2009-0005 | LA-UR-09-0473 |
| Pilot Test Report for Comparing Packer and FLUTe Vapor-Monitoring Systems at Material Disposal Area H, Revision 1 | 02/18/09 | EP2009-0104 | LA-UR-09-0924 |
| Periodic Monitoring Report for Vapor-Sampling Activities for Material Disposal Area H, Solid Waste Management Unit 54-004, at Technical Area 54, First Quarter Fiscal Year 2009 | 04/22/09 | EP2009-0179 | LA-UR-09-2190 |
| Periodic Monitoring Report for Vapor Sampling Activities at Material Disposal Area H, Solid Waste Management Unit 54-004, at Technical Area 54, Revision 1 | 03/18/09 | EP2009-0146 | LA-UR-09-1554 |
| Periodic Monitoring Report for Vapor-Sampling Activities at Material Disposal Area H, Solid Waste Management Unit 54-004, at Technical Area 54, First Quarter Fiscal Year 2009, Revision 1 | 06/19/09 | EP2009-0275/-0276 | LA-UR-09-3829 |
| Periodic Monitoring Report for Vapor-Sampling Activities at Material Disposal Area H, Solid Waste Management Unit 54-004, at Technical Area 54, Second Quarter Fiscal Year 2009 | 07/29/09 | EP2009-0319 | LA-UR-09-4406 |

| Document Title | Date Submitted | Document Catalog Number | LA-UR Number |
|---|---|---|---|
| **MDA K** | | | |
| RFI Report for MDA K, PRS 33-002(a,b,c,d,e) | 09/29/95 | | LA-UR-95-3624 |

| Document Title | Date Submitted | Document Catalog Number | LA-UR Number |
|---|---|---|---|
| **MDA L** | | | |
| IWP (MDA L) | 08/31/03 | ER2003-0504 | LA-UR-03-5998 |
| IWP, Revision 1 (MDA L) | 12/23/03 | ER2003-0766 | LA-UR-03-9120 |
| IWP, Revision 1 (MDA L) | 12/23/03 | ER2003-0766 | LA-UR-03-9120 |
| Investigation Report for Material Disposal Area L, Solid Waste Management Unit 54-006, at Technical Area 54 | 09/13/05 | ER2005-0305 | LA-UR-05-5777 |
| Investigation Report for Material Disposal Area L, Solid Waste Management Unit 54-006, at Technical Area 54, Revision 1 | 03/10/06 | ER2006-0193 | LA-UR-06-1564 |
| Addendum to the Investigation Report for Material Disposal Area L, Solid Waste Management Unit 54-006, at Technical Area 54 | 05/31/07 | EP2007-0264 | LA-UR-07-3214 |
| Periodic Monitoring Report for for Vapor Sampling Activities at Material Disposal Area L, Solid Waste Management Unit 54-006, at Technical Area 54, for Fiscal Year 2007 | 12/10/07 | EP2007-0757 | LA-UR-07-8108 |
| Corrective Measures Evaluation Report for Material Disposal Area L at Technical Area 54 | 01/18/08 | EP2007-0356 | LA-UR-08-0050 |
| Periodic Monitoring Report for Vapor Sampling Activities at Material Disposal Area L, Solid Waste Management Unit 54-006, at Technical Area 54, for First Quarter Fiscal Year 2008 | 05/16/08 | EP2008-0220 | LA-UR-08-3020 |
| Periodic Monitoring Report for Vapor Sampling Activities at Material Disposal Area L for Second Quarter Fiscal Year 08 | 07/28/08 | EP2008-0394 | LA-UR-08-4761 |
| Periodic Monitoring Report for Vapor Sampling Activities at Material Disposal Area L, Solid Waste Management Unit 54-006, at Technical Area 54, for Third Quarter FY08 | 10/27/08 | EP2008-0535 | LA-UR-08-6776 |
| Periodic Monitoring Report for Vapor Sampling Activities at Material Disposal Area L, Solid Waste Management Unit 54-006, at Technical Area 54, for Fiscal Year 2008 | 01/28/09 | EP2009-0013 | LA-UR-09-0516 |
| Periodic Monitoring Report for Vapor Sampling Activities at Material Disposal Area L, Solid Waste Management Unit 54-006, at Technical Area 54, for First Quarter Fiscal Year 2009 | 04/08/09 | EP2009-0190 | LA-UR-09-2078 |
| Periodic Monitoring Report for Vapor Sampling Activities at Material Disposal Area L for Second Quarter Fiscal Year 2009 | 07/29/09 | EP2009-0320 | LA-UR-09-4407 |

| Document Title | Date Submitted | Document Catalog Number | LA-UR Number |
|---|---|---|---|
| **MDA T** | | | |
| Investigation Report for Material Disposal Area T, Consolidated Unit 21-016(a)-99, at Technical Area 21 | 09/18/06 | EP2006-0779 | LA-UR-06-6506 |
| Phase II Investigation Report for Consolidated Unit 21-016(a)-99, Material Disposal Area T, at Technical Area 21 | 11/15/07 | EP2007-0700 | LA-UR-07-7692 |
| Subsurface Vapor-Monitoring Plan for Material Disposal Area T at Technical Area 21 | 10/19/07 | EP2007-0658 | LA-UR-07-7037 |
| Phase II Investigation Report for Consolidated Unit 21-016(a)-99, Material Disposal Area T, at Technical Area 21, Revision 1 | 02/29/08 | EP2008-0101/-0102 | LA-UR-08-1215 |
| Phase III Investigation Work Plan for Material Disposal Area T, Consolidated Unit 21-016(a)-99 | 04/17/09 | EP2009-0187 | LA-UR-09-2140 |
| Periodic Monitoring Report for Vapor-Sampling Activities at Material Disposal Area T, Consolidated Unit 21-016(a)-99, Technical Area 21, Fiscal Year 2008 | 02/13/09 | EP2008-0077 | LA-UR-09-0791 |
| Periodic Monitoring Report for Vapor-Sampling Activities at Material Disposal Area T, Consolidated Unit 21-016(a)-99, Technical Area 21, 1st Quarter 2009 | 07/31/09 | EP2009-0336 | LA-UR-09-4674 |

| Document Title | Date Submitted | Document Catalog Number | LA-UR Number |
|---|---|---|---|
| **MDA U** | | | |
| Historical Investigation Report for Material Disposal Area U, Solid Waste Management Unit 21-017(a)-99, at Technical Area 21 | 11/30/04 | ER2004-0571 | LA-UR-04-7267 |
| Investigation Report (MDA U) | 02/06/06 | ER2005-0923 | LA-UR-05-9564 |
| Revised Investigation Report (MDA U) | 09/08/06 | EP2006-0706 | LA-UR-06-6136 |
| Response to the Notice of Disapproval for the Investigation Report for Material Disposal Area U, Consolidated Unit 21-017(a)-99, at Technical Area 21 | 09/08/06 | EP2006-0705 | LA-UR-06-6136 |

| Document Title | Date Submitted | Document Catalog Number | LA-UR Number |
|---|---|---|---|
| **MDA V** | | | |
| Investigation Report (MDA V) | 10/31/06 | EP2006-0436 | LA-UR-06-6609 |
| Investigation Report for Consolidated Unit 21-018(a)-99, Material Disposal Area V, at Technical Area 21, Revision 1 | 07/16/07 | EP2007-0355 | LA-UR-07-4390 |
| Supplemental Investigation Report for Consolidated Unit 21-018(a)-99, Material Disposal Area V, at Technical Area 21 | 02/08/08 | EP2008-0006 | LA-UR-08-0051 |
| Vadose Zone Subsurface Characterization and Vapor-Monitoring Well Installation Work Plan for Material Disposal Area V, Consolidated Unit 21-018(a)-99 | 05/18/09 | EP2009-0257 | LA-UR-09-3021 |

**Attachment 3**

# Technical Implementation of the Correction Factor Calculation for Tritium in Pore-Gas Data, Revision 1

by
Stanislaw Marczak
WES-EDA, Los Alamos National Laboratory

## Background

Tritium concentration in pore gas is usually measured by adsorbing moisture from the air sample onto the silica gel, distilling and collecting the water from silica gel, and measuring the tritium concentration in the collected water.

Such a procedure, although the best available, carries inherent error resulting from the residual water that is always present on the "dry" silica gel. In effect, this residual water dilutes tritium in the water that has been distilled from the silica gel, thus lowering the results of the measurement.

To account for this dilution, tritium concentration results reported by the analytical laboratory have been recalculated using the correction factor from the equation below (from Whicker et al., 2009):

$$CF = \frac{M_{drysilicagel} \bullet R_{residual} + M_{sample}}{M_{sample}} \qquad \text{Equation 1}$$

Where:

| | |
|---|---|
| $M_{drysilicagel}$ | is the weight of "dry" silica gel before sample moisture adsorption |
| $R_{residual}$ | is the fraction of residual moisture on the "dry" silica gel (typically R=0.064 [Whicker et al., 2009, see the discussion of temperature below]); and |
| $M_{sample}$ | is the weight of the moisture recovered from silica gel or adsorbed on silica gel (obtained from raw analytical data or calculated from field data using the mass of the sample cartridge before and after sample collection). |

Equation 1 can be modified to use the percent moisture value measured by the analytical laboratory. Percent moisture, as used by the laboratory, is defined as

$$p_{\%} = \frac{M_{sample}}{(M_{drysilicagel} + M_{sample})} \bullet 100\%$$

Where:

$M_{drysislcage}+M_{sample}$ represent the weight of the wet silica gel

In fraction form, it is

$$p = \frac{M_{sample}}{(M_{drysilicagel} + M_{sample})}$$

By inverting this equation and dividing the right side by $M_{sample}$, one will derive

$$\frac{1}{p} = \frac{M_{drysilicagel}}{M_{sample}} + 1 \text{ and from here } \frac{M_{drysilicagel}}{M_{sample}} = \frac{1}{p} - 1$$

By modifying Equation 1, one will derive

$$CF = \frac{M_{drysilicagel}}{M_{sample}} \bullet R_{\text{Re}sidual} + 1$$

Using expression for $M_{drysislicagel}/M_{sample}$, one will derive the final Equation 2:

$$CF = (\frac{1}{p} - 1) \bullet R_{residual} + 1 \qquad \text{Equation 2}$$

## Technical/Experimental Constrains on Using Equations 1 and 2

Two factors used in Equations 1 and/or 2 are crucial for the proper computation of the correction factor: (1) fraction of residual moisture on the "dry" silica gel ($R_{residual}$) and (2) percent moisture on the wet silica gel (p or $p_{\%}$). Both depend on how the silica gel is treated before or after sample collection.

The fraction of residual moisture on the "dry" silica gel was experimentally investigated by Whicker et al. (2009). A residual moisture of $R_{residual} = 0.064$ was determined for the "standard" gel preparation temperatures of 110°C and 1000°C to determine hard-bound residual moisture. Both field preparation of the silica gel before sampling and (analytical) laboratory determination of the percent moisture should use a temperature close to 110°C for sample preparation. Based on verbal confirmation from both field contractors and analytical laboratory (ARS), this has been the case for tritium samples analyzed.

Percent moisture on the wet silica gel is determined from the weight of the "wet" silica gel (silica gel with sample adsorbed) and the amount of water recovered during the drying/distillation process. The primary reason for distillation is to recover liquid water for tritium measurement by liquid scintillation. Hypothetically, there are two possibilities when distillation can be stopped: (1) when enough volume of sample is collected for scintillation measurements (5 mL for the analytical laboratory used), and (2) when all loosely bound moisture is removed (see above discussion of temperatures). If case 1 routinely occurred, the percent moisture information would not accurately reflect the

moisture in the sample. Analysis of the raw analytical data indicates usually 10 to 25 mL of water is collected and confirmation from the contract laboratory ensures that case 2 always occurs.

## Implementation

Depending on availability of the data, several different paths may be chosen by Los Alamos National Laboratory (LANL) to calculate the correction factor. The preferred choice for all tritium data collected before July 2009 was method 1 if percent moisture data were available. For historical data where percent moisture data are not available, method 5 is used. For future data, method 3 will be used. Bound water measurements will be done routinely and entered into the calculations.

1. **Percent moisture from the analytical laboratory is available in the database.**

   For gas samples measured for tritium, ER Database (ERDB) reports percent moisture defined by equation: $\%p=(M_{sample}/M_{wet\ silicagel})*100\%$. To calculate the correction factor, users should apply Equation 2. Note that the database lists moisture content as a percentage; the value needs to be changed from percent to a fraction.

   Example:

   Old std result 210
   Old std minimum detectable activity (MDA) 150
   Old std uncertainty 120
   % Moisture 12 => *as a fraction 12/100=0.12*
   ***Correction Factor: CF = (1/0.12-1)*0.064+1=1.469***

2. **Weights of sample cartridge (with adsorbed sample), empty cartridge, and recovered moisture are available <u>from hard copy analytical laboratory.</u>**

   The weight of "wet" silica (silica with moisture adsorbed on the silica) is calculated by subtracting weight of the empty cartridge from weight of the "full" cartridge." Next, the weight of the dry silica ($M_{drysilicagel}$) is calculated by subtracting weight of the recovered moisture ($M_{sample}$) from the weight of the wet silica. The correction factor is calculated using Equation 1. Apply the CF to the standard result, standard uncertainty and standard MDA.

   Example:

   Weight of cylinder with gel 611 g
   Weight of empty cylinder 455 g

*Calculated weight of "wet" gel* *611 – 455=156 g (weight of wet gel may be listed in the raw data)*
Amount of liquid collected 6.8233 g (or mL)
*Calculated weight of "dry" gel* *156 – 6.8233= 149.1767 (weight of wet gel may be listed in the raw data)*

***Correction factor: CF = [(149.1767)*0.064+6.8233]/6.8233 = 2.399***

| | |
|---|---|
| Old std result | 210 |
| Old std MDA | 150 |
| Old std uncertainty | 120 |
| New std result | 210*2.399=503.8 |
| New std MDA | 150*2.399=359.9 |
| New std uncertainty | 120*2.399=287.9 |

3. **Weights of sample cartridge with and without adsorbed sample, empty cartridge (or weight of the dry silica gel inside the cartridge) are available from the field data.**

Correctly recorded field data should allow direct use of method 1.

Example:

Weight of dry gel ($M_{drysilicagel}$) 140 g
(Note: weight of the dry gel can be calculated as a difference between weight of cylinder with gel before sampling – weight of empty cylinder)
Weight of cylinder with gel before sampling 611 g
Weight of cylinder with gel after sampling 621 g
*Calculated weight of collected sample* $M_{sample}$ *= 621 – 611=10 g*
*Bound water is measured as 0.064 for current silica gel batches.*

***Correction factor: CF = [140*0.064+10]/10 = 1.896***

| | |
|---|---|
| Old std result | 210 |
| Old std MDA | 150 |
| Old std uncertainty | 120 |
| New std result | 210*1.896=398.2 |
| New std MDA | 150*1.896=284.4 |
| New std uncertainty | 120*1.896=227.5 |

4. **Weights of sample cartridge with and without adsorbed sample are available from the field data (but no weight of empty cartridge).**

In this case one has to assume the weight of the "dry" silica gel ($M_{drysilicagel}$) equals 135 g. The remainder of the calculation follows that in method 3 above.

5. **When field silica gel weight/percent moisture data are unavailable, assume CF = 2.**

   A correction factor of 2 was determined using a Monte Carlo analysis of 2 yr of weight/percent moisture data (Whicker et al., 2009).

## Justification of the Implementation Priorities

Two major factors need to be considered when choosing implementation of the correction factor computation: the trustworthiness of the data and the availability of the necessary data.

For past tritium measurements, there was no formal requirement to collect silica field weights. Therefore, silica gel field weights are only available for approximately 50% of samples collected before July 2009. In addition, without a formal requirement, there were no quality assurance checks implemented for silica gel field weights. In contrast, the percent moisture data for past tritium measurements were collected by certified analytical laboratories required to follow good analytical laboratory practices. The percent moisture data were available for 90% of the tritium measurements collected before July 2009. Based on this comparison, the percent moisture data available provide a more defensible method to correct pre–July 2009 tritium measurements.

For post–July 2009 tritium pore-vapor measurements, silica gel weights will be used to determine the correction factor, following Equaltion 1. The silica gel weights provide a more direct measurement to the correction factor as the initial weight of the silica gel and the amount of sample moisture are both measured.

## Reference

Whicker, J.J., J.M. Dewart, S.P. Allen, W.F. Eisele, M.C. McNaughton, and A.A. Green, June 17, 2009. "Corrections for Measurement of Tritium in Subterranean Vapor Using Silica Gel," Los Alamos National Laboratory document LA-UR-09-03837, Los Alamos, New Mexico. (Whicker et al., 2009)

**Attachment 4**

# Corrections for Measurements of Tritium in Subterranean Vapor Using Silica Gel

**Jeffrey J. Whicker**[1,3]
**Jean M. Dewart**[1]
**Shannon P. Allen**[2]
**William F. Eisele**[1]
**Michael C. McNaughton**[1]
**Andrew A. Green**[1]

**LA-UR-09-06230**
**ERID 106983**

[1] Los Alamos National Laboratory, Environmental Programs, Mail Stop M992, Los Alamos, NM 87545
[2] Los Alamos National Laboratory, Environmental Programs, Mail Stop J963, Los Alamos , NM 87545
[3] Corresponding author, jjwhicker@lanl.gov; phone 505-667-2610; fax 505-665-8787

## Abstract

Hazardous contaminants buried within vadose zones can accumulate in soil gas. The concentrations and spatial extent of these contaminants are measured to evaluate potential transport to ground water for public risk evaluation. Tritium is an important contaminant found in and monitored for in vadose zones across numerous sites within the United States nuclear weapons complex, including Los Alamos National Laboratory. The extraction, collection, and laboratory analysis of tritium from subterranean soil gas presents numerous technical challenges that have not been fully studied. Particularly, the lack of soil moisture in the soil gas in the vadose zone makes it difficult to obtain enough sample moisture (e.g., >5 g) to provide for the required sensitivity, and often, only small amounts of moisture can be collected. Further, although silica gel has high affinity for water vapor and is prebaked prior to sampling, there is still sufficient residual moisture in the prebaked gel to dilute the relatively small amount of sampled moisture; thereby, significantly lowering the "true" tritium concentration in the soil gas. This paper provides an evaluation of the magnitude of the bias from dilution, provides methods to correct past measurements by applying a correction factor (*CF*), and evaluates the uncertainty of the *CF* values. For this, ten-thousand Monte Carlo calculations were performed and distribution parameters of *CF* values were determined and evaluated. The mean and standard deviation of the distribution of *CF* values were $1.53 \pm 0.36$, and the minimum, median, and maximum values were 1.14, 1.43, and 5.27, respectively.



Keywords: tritium, soil gas monitoring, risk assessment, ground water.

# Introduction

### *Background*

Past operations within the nuclear weapons complex in the United States have resulted in environmental contamination at numerous locations, including Los Alamos National Laboratory (LANL) in New Mexico (NAP 1989). While the most highly contaminated sites have been remediated, LANL continues to perform environmental sampling to ensure public and environmental health and to demonstrate compliance with existing regulations (LANL 2007). One part of these efforts includes extraction of soil gas from subterranean monitoring wells (LANL 2009). These monitoring wells are used as access ports to sample bedrock and soil gas at different depths within the vadose zone where samples are taken for measurement of a variety of chemical and radiological contaminants, including tritium. Extraction and measurement of tritium in subterranean samples presents numerous technical challenges regarding the sampling, measuring, and interpretation of tritium concentration measurements in the soil gas.

Though tritium contamination in either the liquid or gas phase in the vadose zone does not generally represent a direct ingestion or inhalation dose pathway for humans or other biota, sampling of soil gas is performed for several important reasons. Firstly, contamination from most spills and buried waste initially enters the vadose zone, and detection of contamination in the soil gas or liquid is one of the first indicators of a breach of containment. Second, and important for risk assessment, the soil gas concentration data at different well depths is used to identify and establish temporal and spatial patterns in concentrations and to investigate plume transport. The major concern is to assess the potential for the plume to reach groundwater where the tritiated water

would present a direct dose pathway to people through drinking water. Finally, the measurements can be also used to test and calibrate migration models for predicting the transport of contaminants to groundwater (Till and Grogan 2008).

***Measurement Procedure and Calculations***

A procedure (LANL 2009) was developed to ensure consistency in sampling soil gas in the vadose zone for tritium. The procedure generally follows the standard protocol for soil gas monitoring found in ASTM D5314-92 (ASTM 2006). The general sampling process includes using air pumps to purge sampling lines, extraction of the soil gas from the bed rock and transporting the sample to the surface where the soil gas is passed through about 135 g of prebaked silica gel contained within a sampling tube. The sampling continues until about 5 g (i.e., 5 mL) of soil gas moisture is collected. Thereafter, sampling, the tubes are immediately sealed and sent to an analytical laboratory where the collected moisture is driven off the silica gel by heating and then analyzed for tritium using liquid scintillation counting. Results are reported in Becquerels ($Bq$) per liter ($L$) and represent the concentration of tritium in the extracted vapor at a particular depth in the vadose zone. Eqn. 1 shows formula for the tritium concentration from the extracted vapor condensate:

$$C(Bq/L) = \frac{A}{V} = \frac{A}{M_E \div \rho_{water}} \quad \text{(Eqn. 1)}$$

where: $A$ is the amount of radioactivity of tritium in the moisture (units of Bq), and

$V$ is the volume of the liquid in the sample analyzed (unit of L),

$M_E$ is the mass of the liquid extracted (unit of g), and

$\rho$ is the density of water (unit of g $cm^{-3}$).

There are several potential sources of uncertainty in Eqn. 1. There is random error in the radioactivity measurements ($A$), the error of the measurements of mass of the sampled moisture ($M_E$) is a few percent, and the density of water ($\rho$) is considered to be a constant. However, the largest potential error is less obvious and is based on the assumption that the mass of the water extracted during laboratory analysis is solely from the vapor sampled, that is, we assume no bound water in the prebaked silica gel. This assumption has previously been shown to be wrong, even with prebaking.

Patton et al. (1997) found that silica gel baked in an oven at over $\geq 100^{\circ}$ C for extended time periods still contained substantial amounts of tightly bound water. The amount of residual moisture depends on the nature of the silica gel, but the amount is large enough to significantly affect results (Rosson et al. 2000, Guthrie et al. 2001) leading to underestimation of tritium releases to the environment (Simpkins and Hamby 1997). The error in the assumption occurs when the HTO in the sample undergoes isotopic exchange, or mixing, with the bound $H_2O$ in the silica gel. This "dilution" reduces the tritium concentration in the extracted liquid, which is used to measure concentrations.

Correction, for residual moisture, to tritium concentration measurements is required. First, the mass of the liquid extracted from the silica gel ($M_E$) will be a combination of the sampled mass ($M_S$) and the residual moisture ($M_R$) in the silica gel, as shown in Eqn. 2.

$$M_E = M_s + M_R \quad \text{(Eqn. 2)}$$

Ideally, $M_E$ would equal $M_S$. However, if one makes the reasonable assumption that $M_R$ contains a relatively small amount of tritium [background tritium concentrations in freshwater and water vapor are about 1 Bq $L^{-1}$ (NCRP 1979, UNSCEAR 2000)], and that the tritium in the sample mixes thoroughly with the residual moisture, then Eqn. 3 shows how residual moisture dilutes the sample with "clean" water and results in a measured tritium concentration, $C_M$, that is biased low.

$$C_M(Bq/L) = \frac{A}{V} = \frac{A}{M_E \div \rho_{water}} = \frac{A}{(M_S + M_R) \div \rho_{water}} \quad \text{(Eqn. 3)}$$

To correct for residual moisture in the sample, the mass of the residual water needs to be determined. The mathematical formulas to provide corrected concentrations, $C_C$, are shown in Eqns. 4 and 5.

$$C_C(Bq/L) = \frac{A}{(M_S + M_R) \div \rho} \times \frac{(M_S + M_R)}{M_S} \quad \text{(Eqn. 4)}$$

$$C_C(Bq/L) = \frac{A}{(M_S + M_R) \div \rho} \times CF \quad \text{(Eqn. 5)}$$

Here, $CF$ is the correction factor that adjusts the measured tritium concentrations to account for residual moisture in the silica gel. The mass of the sampled water, $M_S$, is measured as the difference in masses of the cartridge containing the silica gel before and after sample collection. The mass of the residual moisture can be determined by knowing the fraction of residual moisture, by mass, in the prebaked silica gel prior to sampling.

$$M_R = M_{SilicaGel} \times F_{RM} \quad \text{(Eqn. 6)}$$

$F_{RM}$ is the fraction of the mass of the prebaked silica gel due to residual moisture. The correction factor, $CF$, then becomes:

$$CF = \frac{\left(M_{SilicaGel} \times F_{RM}\right) + M_S}{M_S}, \quad \text{(Eqn. 7)}$$

which is substituted into Eqn. 5 to correct samples for the dilution due to residual moisture. $M_{SilicaGel}$ and $M_S$ are measured in the laboratory per procedure, but measurement of the fractional mass of the moisture is needed for the correction.

**Purpose of Study**

Measurement techniques for sampling tritium in subterranean soil gas have not been thoroughly investigated, especially relative to sampling atmospheric air for tritium (Eberhart 1999). A specific concern was that dilution of samples with residual moisture in the prebaked silica gel can result in significant systematic biases in the tritium measurements. Other studies have shown that this correction can be significant and can

vary with silica gel type, amount of moisture collected, and laboratory procedures (Eberhart 1999, Rosson et al. 2000), but this had not been investigated for subterranean soil gas measurement techniques. Correction of the tritium concentrations is particularly important for subterranean soil gas measurements because the soil gas is relatively dry and generally only small amounts of moisture are collected, which results in larger errors.

Sample specific data can be used to correct future measurements using Eqn. 7 on an individual basis; however, it was also important to assess the magnitude of correction factors for uncorrected historical data. In most of these cases, the required data to make these corrections were not collected. Therefore, the primary tasks of this study were to analyze the potential error, determine the correction factors (i.e., Eqn. 7), and investigate the uncertainty of the correction factors to be used for these tritium measurements. These corrections are required for more accurate measurement and analysis of tritium concentrations in subterranean soil gas and the assessment of the potential radiological hazards associated with the tritium.

## METHODS

### *Determination of Residual Moisture ($F_{RM}$) in Silica Gel*

A series of measurements (n = 18) were made of the residual moisture mass in silica gel that was used to collect soil gas vapor for tritium analysis. Soil gas measurements of tritium at LANL are made by two environmental contractors, and because each contractor uses a different silica gel, nine measurements were conducted on each gel type to allow assessment of intra- and inter-gel variability.

The following procedure was used for these measurements. First, silica gel from both contractors was prebaked separately at a temperature of 105° C for over two days, as required in the standardized procedures. The prebaked silica gel samples from both contractors were quickly separated into individual samples with masses of approximately 1, 2, 3, and 5 g. The prebaked masses ($M_{before}$) were recorded; then, samples were put in a furnace for complete denaturing. For denaturing, all samples were placed into a furnace at a temperature of 1000° C for 2 hours, and the final mass of the denatured gel ($M_{final}$) recorded. The residual/bound moisture fraction by mass was calculated as shown in equation 8.

$$F_{RM} = \frac{m_{before} - m_{final}}{m_{before}} \qquad \text{(Eqn. 8)}$$

***Uncertainty Analysis for correction for residual moisture in silica gel***

Analysis of the uncertainty of the correction factor, *CF*, was done using Monte Carlo simulation techniques (Till and Grogan 2008) using Crystal Ball software[3]. The Monte Carlo technique allows propagation of errors from each variable through the final calculations of *CF*. The distribution of each parameter in Eqn. 7 was determined based either on actual measurements or an assumed distribution in cases where empirical data was absent. The first parameter is the mass of the sample collected ($M_S$). Over 150 measurements of $M_S$ collected from 2007 and 2008 field logbooks were analyzed and $M_S$ ranged from about 2 to 46 g with a median of 15 g. Therefore, in the Monte Carlo simulations we assumed a triangular distribution with 2 g, 15 g, and 46 g as the

[3] Oracle Software, 1515 Arapahoe St. Suite 1300, Denver, CO 80202

minimum, most likely, and maximum masses of collected samples, respectively. For the second parameter, the mass of the silica gel ($M_{SilicaGel}$), actual measurements have not been previously made so we assumed the typical amount of 135 g ± 13.5 g. This amount is based on the stated mass of silica gel in a cylinder, as written in the procedure (LANL 2006), with a 10% error. A normal distribution of fractional moisture content by mass ($F_{RM}$) was assumed and was based on the mean and standard deviations measurements made during the denaturing process. The values used for the distribution of $F_{RM}$ were 6.4% ± 0.3% (further details are in the Results section). Ten-thousand Monte Carlo calculations were run and the final distribution for *CF* was determined from these results. As an additional test, the Monte Carlo generated distribution was compared to the summary statistics from 438 independent *CF* results that were calculated from actual vapor measurements made at several boreholes within LANL.

## Results

The percent bound moisture for the silica gel used by the two environmental contractors was similar, with means and standard deviations of 6.5 ± 0.25% and 6.1 ± 0.14% (Table 1). The combined mean and standard deviation was 6.4 ± 0.3 %. There was no statistically significant difference between the two types of silica gels used by the contractors, so both sets of data were combined in the statistical analysis and all data are shown in Fig. 1, which shows the results in terms of water loss as a function of the initial mass of the silica gel. The regression slope was slightly over 6% residual moisture mass per gram of silica gel. For example, a sample canister with 100 g of silica gel would

contain about 6 g of residual moisture in the canister. Given that sampling of vapor stops when about 5 g of vapor moisture is collected, the relative amount of residual moisture in the silica gel is enough to dilute the sample making correction important.

A typical correction factor (*CF*) can be estimated using Eqn. 7 assuming the initial mass of the silica gel was 135g, the fractional amount of moisture in the silica gel was 0.064, and the mass of the sampled vapor was 15 g. The correction factor becomes 1.57, as shown in Eqn. 9.

$$CF = \frac{(135g \times 0.064) + 15g}{15g} = 1.57 \qquad \text{(Eqn. 9)}$$

However, each individual variable in Eqn. 9 has an associated uncertainty. The overall uncertainty of the *CF* was determined through propagation of the individual uncertainties using Monte Carlo simulations from Crystal Ball, as described in the Methods section. The resulting distribution of values for *CF* is presented in Fig. 2. The mean and standard deviation of the distribution of *CF* values in Fig. 2 was 1.53 ± 0.36, and the minimum, median, and maximum values were 1.14, 1.43, and 5.27, respectively. Ninety-five percent of the *CF* values were less than about 2. The comparison distribution of *CF* values derived from an actual and independent set of measurements (n=438) showed a similar distribution to the Monte Carlo derived values with a mean and standard deviation of 1.66 ± 0.325. The minimum, median, and maximum *CF* values for the measurements were 1.17, 1.57, and 3.32, respectively. The *CF* value for the 25$^{th}$ percentile was 1.44 and was 1.82 for the 75$^{th}$ percentile.

## Discussion and Conclusions

Correction factors for subterranean measurements of tritium in soil gas were determined. Application of these corrections would improve their accuracy and increase the inherent value of this data for future uses. The measurements of moisture in silica gel reported here resulted in a median correction factor of 1.43, and ranged from 1.14 to 5.27. These correction factors are similar to those found by Rosson et al. (2000) and Guthrie et al. (2001), though those studies did not fully assess the uncertainties in the correction factors, as was done here.

One of the main implications of the study is that the magnitude of the correction factor decreases non-linearly as the amount of moisture in the sample increases, as shown in Fig. 3. Further, the sensitivity (rate of change in CF with changes in sample mass) decreases with increased sample mass. Combined, this shows that larger samples need less correction and that the uncertainty would be less. Operationally, there is a balance that has to be struck during sampling because sampling in dry bedrock requires very long sampling times, which can be inconvenient and costly. Optimization of the sample times and mass is appropriate, and the relationship shown in Fig. 3 can help with decisions on required sampling times and masses. For example, Fig. 3 shows that the current limitation of having a minimum of a 5 g sample seems appropriate.

There are several important assumptions made that affect the correction factor, as described in this report. The first is that it is assumed that the tritium in the sampled HTO is fully mixed with the residual moisture in the silica gel. That is, the isotopic exchange is complete. Rosson et al. (2000) showed that this is a reasonable assumption

though they found that amount of exchangeable water in the silica gel could be slightly higher (about 10%) than the mass of water content in the silica gel (determined through denaturing) possibly due to unaccounted alterations in hydroxyl groups or residual moisture during denaturing. A second assumption is that there is no isotopic difference in the concentrations of HTO and $H_2O$ in the water evaporated during the processing of the sample in the laboratory. Rosson et al. (2000) showed that this is a reasonable assumption, especially for the higher temperatures used to drive the moisture off the silica gel, and the impact of the isotope effect for this process is only a few percent. The isotope effect for evaporation is much larger at lower temperatures (e.g., $10^{\circ}$ C) and needs to be accounted for when calculating concentrations in soil water from subterranean soil gas measurements (Price 1958).

In summary, the impact of residual bound moisture on tritium measurements in soil vapor is sufficient to warrant correction. This paper provides a technique to calculate the distribution of correction factors (CFs) that can be used to correct historical data even in cases where needed information is missing. The calculations also show that the correction factor is largest for samples with the least amount of collected moisture and will approach one as more sample mass is collected, but the realistic amounts of moisture collected under normal sampling times require correction. Ultimately, this correction will provide more accurate data for measurement interpretation and risk assessment for public exposures.

## Acknowledgements

This work was supported by the United States Department of Energy under contract DE-AC52-06NA25369. The authors would like to express their thanks to Ron Rager, Craig Eberhart, and Chris Ecohawk for their technical guidance and support during this project.

## References

American Society for Testing and Materials (ASTM) (2006). Standard Guide for Soil Gas Monitoring in the Vadose Zone. ASTM D5314.

Eberhart, C.F. (1999). Using absolute humidity and radiochemical analyses of water vapor samples to correct underestimated atmospheric tritium concentrations. Los Alamos National Laboratory report LA-UR-99-1107.

Guthrie, E.B., Shen, N.C., & Bandong, B.B. (2001) Isotope exchange and fractionation corrections for extraction of tritiated water in silica gel by freeze-drying techniques. Lawrence Livermore National Laboratory Report UCRL-ID-148610.

Los Alamos National Laboratory (LANL). (2006). Sampling of ambient airborne tritium. LANL procedure ENV-MAQ-204, R13.

Los Alamos National Laboratory (LANL). (2007). Environmental Surveillance at Los Alamos during 2007. Los Alamos National Laboratory report LA-14385-ENV.

Los Alamos National Laboratory (LANL). (2009). Sampling for sub-atmospheric air. LANL Procedure EP-ERSS-SOP-5074.

National Academy Press (NAP). (1989). The nuclear weapons complex: Management for health, safety, and the environment. National Academy Press: Washington, D.C.

National Council on Radiation Protection (NCRP). (1979). Tritium in the environment. NCRP Report no. 62.

Okada, S., & Momoshima, N. (1993). Overview of tritium: characteristics, sources, and problems. Health Physics 65:595-609.

Patton, G.W., Cooper, A.T., & Tinker, M.R. (1997). Ambient air sampling for tritium-determination of breakthrough volumes and collection efficiencies for silica gel. Health Physics 72:397-407.

Price, A.H. (1958). Vapour pressure of tritiated water. Nature 181: 262.

Rosson, T., Jakiel, R., Klima, S., Kahn, B., & Fledderman, P. (2000). Correcting tritium concentrations in water vapor monitored with silica gel. Health Physics 78: 68-73.

Simpkins, A.A., Hamby, D.M. (1997). Predicted vs. measured tritium oxide concentrations at the Savannah River Site. Health Physics 72:179-185.

Till, J.E., & Grogan, H.A. (eds). (2008). Radiological risk assessment and environmental analysis. Oxford University Press: New York, New York.

United Nations Scientific Commission on the Effects of Atomic Radiation (UNSCEAR). (2000). Report of the United Nations Scientific Committee on the Effects of Atomic Radiation to the General Assembly.

**Figure Captions**

Figure 1. Decrease in water mass as a function of amount of silica gel in sample before denaturing in the high temperature oven.

Figure 2. Distribution of values for the correction factor.

Figure 3. Relationship between the correction factors, calculated using average values for residual moisture and mass of silica gel, and the mass of sampled moisture.

Table 1. Results of measurements made to determine the percent of residual, bound moisture in silica gel following prebaking. Results include samples from both LANL contractors.

| Crucible | Mass of empty crucible (g) | Mass of crucible w/pre-denatured gel (g) | Net mass of gel (g) | Cruc. w/ denatured gel (g) | Mass of water loss (g) | Percent bound water |
|---|---|---|---|---|---|---|
| | | | **Contractor 1** | | | |
| 1 | 49.3912 | 50.4388 | 1.0476 | 50.3682 | 0.0706 | 6.74 |
| 2 | 48.4071 | 49.4224 | 1.0153 | 49.3522 | 0.0702 | 6.91 |
| 3 | 52.2148 | 53.2605 | 1.0457 | 53.1904 | 0.0701 | 6.70 |
| 4 | 52.7999 | 55.8038 | 3.0039 | 55.6114 | 0.1924 | 6.41 |
| 5 | 51.6778 | 54.6539 | 2.9761 | 54.4636 | 0.1903 | 6.39 |
| 6 | 51.845 | 54.8281 | 2.9831 | 54.6384 | 0.1897 | 6.36 |
| 7 | 51.7259 | 56.7239 | 4.998 | 56.413 | 0.3109 | 6.22 |
| 8 | 49.3898 | 54.3796 | 4.9898 | 54.069 | 0.3106 | 6.22 |
| 9 | 48.4061 | 53.3839 | 4.9778 | 53.0701 | 0.3138 | 6.30 |
| | | | | | **AVERAGE** | **6.47** |
| | | | | | **STD** | **0.25** |
| | | | **Contractor 2** | | | |
| 1 | 52.2133 | 53.2349 | 1.0216 | 53.1747 | 0.0602 | 5.90 |
| 2 | 52.7987 | 53.7927 | 0.994 | 53.7314 | 0.0613 | 6.17 |
| 3 | 51.6764 | 52.6739 | 0.9975 | 52.6126 | 0.0613 | 6.15 |
| 4 | 51.8433 | 54.8441 | 3.0008 | 54.6586 | 0.1855 | 6.18 |
| 5 | 51.7246 | 54.7121 | 2.9875 | 54.5259 | 0.1862 | 6.23 |
| 6 | 49.3912 | 51.3687 | 1.9775 | 51.2461 | 0.1226 | 6.20 |
| 7 | 48.4074 | 53.3855 | 4.9781 | 53.0817 | 0.3038 | 6.10 |
| 8 | 52.2141 | 57.2201 | 5.006 | 56.921 | 0.2991 | 5.97 |
| 9 | 52.7997 | 57.7492 | 4.9495 | 57.4605 | 0.2887 | 5.83 |
| | | | | | **AVERAGE** | **6.08** |
| | | | | | **STD** | **0.14** |

**Figure 1.**

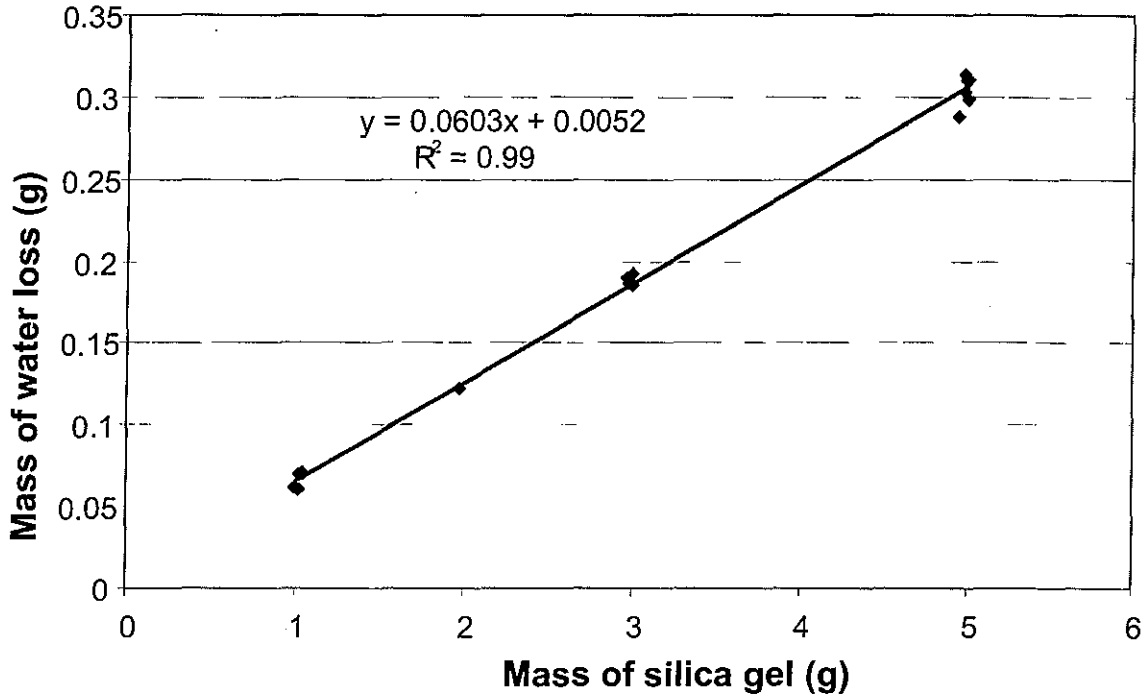

0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
y = 0.0603x + 0.0052
R2 = 0.99
Mass of water loss (g)
0
1
2
3
4
5
6
Mass of silica gel (g)

**Figure 2.**

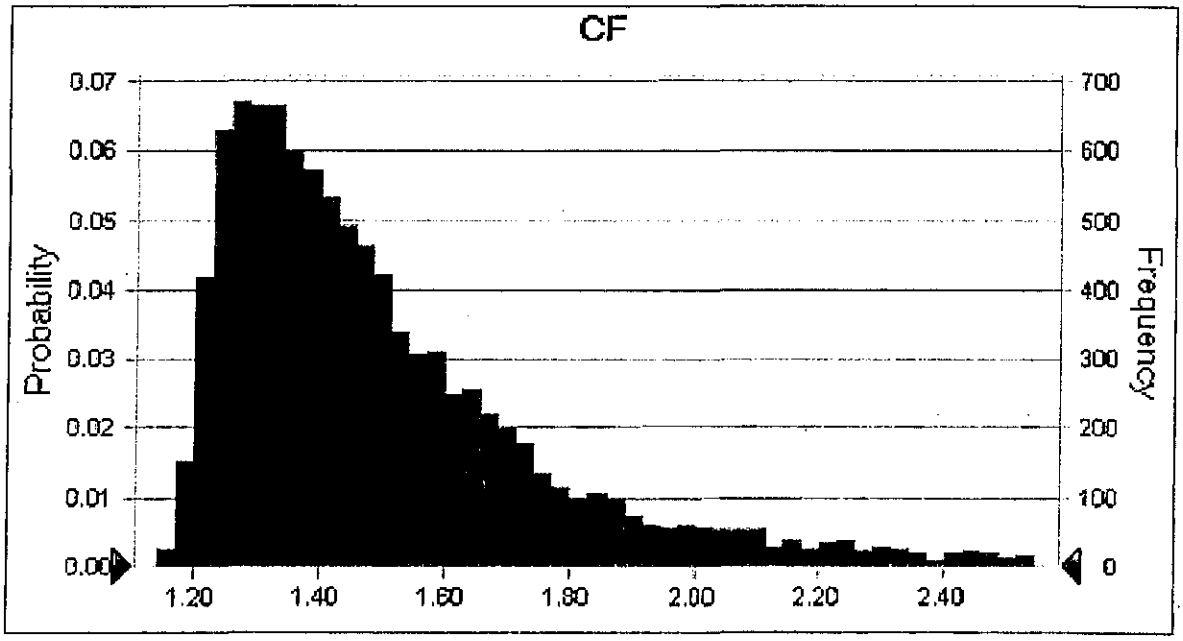
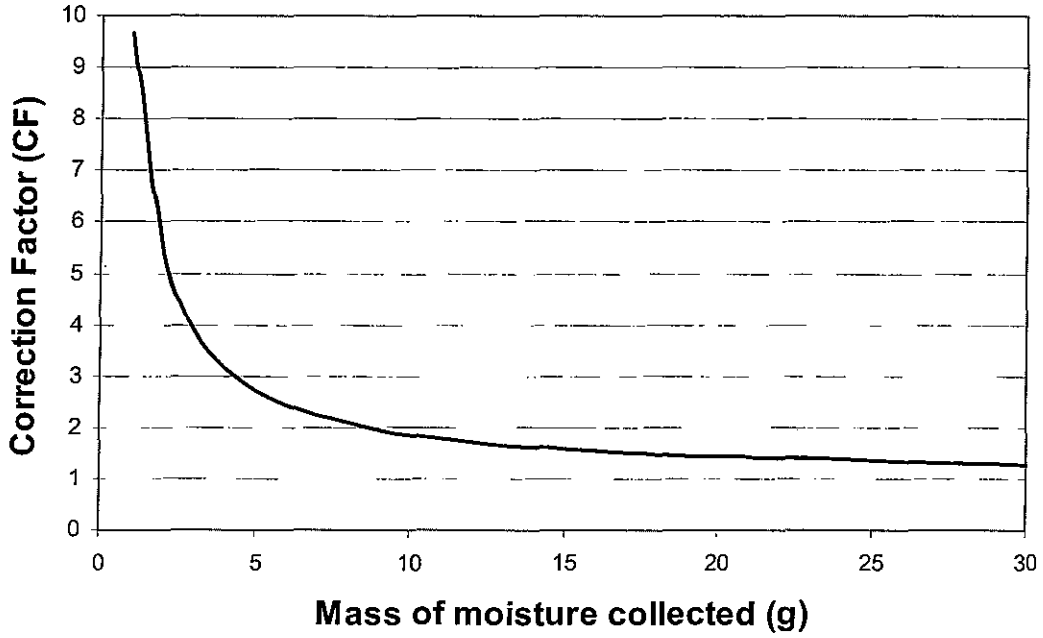

CF
Probability
Frequency
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
700
600
500
400
300
200
100
0
1.20
1.40
1.60
1.80
2.00
2.20
2.40

**Figure 3.**


Correction Factor (CF)
10
9
8
7
6
5
4
3
2
1
0
0
5
10
15
20
25
30
Mass of moisture collected (g)